ORIGINAL ARTICLE

Micellization Studies of Dicationic Gemini Surfactants (m-2-m Type) in the Presence of Various Counter- and Co-Ions

Jeenat Aslam · Umme Salma Siddiqui · Wajid Husain Ansari · Kabir-ud-Din

Received: 30 July 2012/Accepted: 6 February 2013/Published online: 7 March 2013 © AOCS 2013

Abstract Salts have the ability to influence the water activity and self-association of ionic micelles. In the present case, gemini surfactants; ethanediyl- α , ω -bis (dimethyl alkyl ammonium bromide) (referred to as m-2m, m = 10, 12, 14) are synthesized and their micellization study in aqueous medium in presence of monovalent inorganic (NaBr, NaNO₃, NaCl, KCl, LiCl) and organic salts (NaTos, NaBenz, NaSal) at 303 K is systematically investigated by conductometric and tensiometric methods. All the salts have the tendency to lower the critical micelle concentration of the surfactants. The effect of inorganic salts on the micellization properties has been found to obey the Hofmeister series. Organic salts reduce the CMC more effectively as compared to inorganic salts. The theoretical models of Rubingh and Rosen have been used to compare the results and obtain the interaction parameters, minimum area per molecule, surface excess, mixed micelle composition, activity coefficients and free energies of micellization/adsorption.

Keywords Cationic gemini surfactants \cdot Critical micelle concentration \cdot Mixed micelles \cdot Synergism \cdot Counterion \cdot Coion

Electronic supplementary material The online version of this article (doi:10.1007/s11743-013-1453-5) contains supplementary material, which is available to authorized users.

J. Aslam · U. S. Siddiqui (⊠) · W. H. Ansari (⊠) · Kabir-ud-Din Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India e-mail: drsalsidd@gmail.com

W. H. Ansari e-mail: wajidhusain.chem@gmail.com

Introduction

Over the last few decades, a new type of surfactant, gemini or dimeric, has received keen attention worldwide. The reason is that these surfactants possess superior physicochemical properties over conventional surfactants. They are made up of two amphiphilic moieties connected at the level of the headgroups by a spacer group. Owing to their unique structure, they have much lower critical micelle concentrations (CMC), better wetting, foaming, solubilizing abilities, and unusual aggregation morphologies [1–7]. Gemini surfactants of the type m-*s*-m are generally used for most of the research studies, where m is the carbon number in the alkyl chain length and *s* is the carbon number in the spacer chain length. The stereochemistry of the spacer and the alkyl chain length of gemini surfactants play significant roles in understanding the micellization phenomenon [3–7].

Gemini surfactants with short spacers have a shorter distance between the two alkyl chains, a characteristic which enhances the hydrophobic interaction, restricts hydrophobic hydration and minimizes electrostatic repulsion between the two alkyl chains of gemini molecule leading to low CMC values. As a result, they reflect higher functionalities that could lead to a reduction in their consumption. This is a point worth mentioning regarding their environmental toxicity. These surfactants are capable of forming worm-like micelles, causing micellar growth at low concentrations [8, 9].

The self-aggregation or micellization of surfactants in solution is a well-known phenomenon, which depends on the amphiphilic species and on the conditions of the system in which they are dissolved. It is mainly controlled by two opposing tendencies: the removal of the nonpolar hydrocarbon chains from the aqueous environment and the repulsions among polar head groups, which is reasonably pacified by the presence of counterions to the surface of the micelle. The narrow concentration range over which surfactant solutions show an abrupt change in the physicochemical properties is called the CMC, where micelle formation starts taking place [10, 11]. Thus, the characteristics of these aggregates are easily controlled by the changes in the surfactant molecular structure and the solution conditions, such as pH, concentration, temperature, additives, etc.

Depending on size and nature of counterions, micellar morphology can be controlled by addition of salts [12, 13]. Salts have the tendency to lower the CMC of ionic surfactants. In the past, the effect of salts on the micellization process has been investigated in the light of Hofmeister series (HS), where ions have been classified in order of their ability to salt-out or salt-in proteins [14].

The properties of ionic surfactants possessing small counterions, such as halides, generally follow HS, which is related to the polarizability of ions. Hydrophobic/chaotropic counterions are bound more strongly to the micellar surface than hydrophilic/kosmotropic counterions. As compared to kosmotropic anions, chaotropic anions are more effective in promoting the micellar growth of ionic surfactants [15, 16]. Therefore, a decrease of hydrophobicity (polarizability) of the counterions generally reduces its affinity towards ionic micellar surfaces and the tendency to form ion pairs leads to higher ionization degrees. This disfavors the micellization process and gives higher CMC values.

However, in the case of polyatomic ions, the steric effects and inter/intramolecular interactions play important roles in the aggregation behavior of amphiphiles. A literature review [17–20] has thrown light on the micellization of surfactants in the presence of various anions such as halides or alkylsulfonates, as well as benzoate derivatives. It was observed that the CMC and ionization degree of micelles do not depend on a single known parameter or the nature of the counterion (i.e., ion size, polarizability, or ion hydrophilicity, etc.).

Thus, for a proper understanding of the fundamental micellar solution properties, we report micellization studies of more efficient gemini surfactants having a shorter spacer (m-2-m) (Scheme 1) in the presence of inorganic and organic salts by conductometric and tensiometric techniques. The small inorganic counterions (Br⁻, Cl⁻, NO₃⁻, which are principally from the Hofmeister series) and aromatic counterions (Tos⁻, Benz⁻, Sal⁻, Scheme 2) have been taken into account. In order to evaluate the effect of alkyl chain length variation (m = 10, 12, 14) on the micellization process, we have kept the spacer chain length (s = 2) and headgroups the same in all the geminis. The gemini surfactants used in the study have proven themselves to be good inhibitors of iron corrosion in a



Scheme 1 Protocol for the synthesis of m-2-m geminis



sodium salicylate (Sal⁻) sodium benzoate (Benz⁻) sodium tosylate (Tos⁻)



hydrochloric acid medium. Due to the formation of a protective layer on the electrode surface [21], they show maximum inhibition efficiency near their CMC values.

The micellization behavior of gemini surfactants is significantly affected by the presence of electrolytes and the effect is generally attributed entirely to the interaction of counterions with the gemini micelles, as reported in the literature [19, 22–25]. There are, furthermore, some reports [26, 27] which indicate that co-ions can also affect the micellization phenomenon of ionic surfactants.

Experimental

Materials

The chemicals 1-bromodecane (Sigma-Aldrich, USA, ≥ 98 %), 1-bromododecane (Sigma-Aldrich, USA, ≥ 97 %), 1-bromotetradecane (Sigma-Aldrich, USA, ≥ 98 %), *N*, *N*, *N*, *N*-tetramethylethylenediamine (s. d. fine-Chem., Mumbai, ≥ 99 %), propanol (E. Merck, Mumbai, ≥ 99 %), NaNO₃ (Merck, Mumbai, ≥ 98 %), NaBr (s. d. fine-Chem., Mumbai, ≥ 98 %), NaCl (s. d. fine-Chem., Mumbai, ≥ 98 %), NaCl (s. d. fine-Chem., Mumbai, ≥ 98 %), Sodium salicylate NaSal (Fluka, Switzerland, ≥ 99 %), sodium tosylate NaTos (Fluka, Switzerland, 298 %), and sodium benzoate NaBenz (Merck, Germany, 99.5 %) were used as received. Water was distilled twice over alkaline KMnO₄ in an all-glass still.



Fig. 1 Variation in surface tension versus concentration for the pure gemini surfactants at 303 K $\,$

Synthesis and Characterization of Gemini Surfactants

A mixture of *N*, *N*, *N*, *N*-tetramethylethylenediamine with a corresponding bromoalkane in dry propanol was refluxed with continuous stirring for 48 h to synthesize ethanediyl- α, ω -bis(dimethylalkylammonium bromide) (10-2-10, 12-2-12, 14-2-14) gemini surfactants [28, 29] (Scheme 1). After evaporating the solvent, the residue was recrystallized in a mixture of acetone and ethanol three times to give a white product. The compound was dried in an oven for 3 days until constant weight was attained. The yields were almost quantitative, 90–97 %. The purities were checked via ¹H-NMR spectra recorded in CDCl₃ solution with BRUKER AVANCE 300 MHz spectrometer.

¹H NMR (300 MHz, CDCl₃) (m-2-m): $\delta = 0.9$ [*t*, 6H, 2(CH₃)], 1.26–1.38 [*m*, 36 H, (–CH₂–) alkyl chain], 1.81 [*m*, 4H, CCH₂CN⁺ alkyl chain], 3.50 [*s*, 12H, (CH₃)₂N⁺], 3.69 [*t*, 4H, CCCH₂N⁺ alkyl chain], and 4.67 ppm [*s*, 4H, N⁺CH₂CH₂N⁺].

Conductometric Measurements

The conductance measurements were made with a Systronics conductivity meter 306, using a dip cell (cell constant 0.1 cm^{-1}). The experiments were performed at 303 K by circulating water through a jacketed cell holding the solutions under study. Concentrated stock solutions of surfactants were prepared in double-distilled water or in salt of desired concentration. These stock solutions were added to a known quantity of distilled water or salt solution of concentration as in the stock. The conductivity at each concentrated surfactant stock solution to the thermostated solution.

Surface Tension Measurements

The surface tension measurements were done by a Krüss 11 Tensiometer by the platinum ring detachment method. Concentrated stock solution of surfactant prepared in different fixed concentrations of salt solution was added in installments to a known quantity of distilled water (or salt solution of fixed concentration as taken in the stock) in a vessel and the readings were taken after thorough mixing and temperature equilibration. The corrections to the γ values were made according to the procedure of Harkins and Jordan in-built in the instrument software. The accuracy of the γ value measurements was within $\pm 0.1 \text{ mNm}^{-1}$.

Results and Discussion

The surface tension of water decreases with an increase in surfactant concentration. At low concentrations, the surfactant molecules have the tendency to adsorb at the liquid/ air interface until the surface of the solution is totally occupied and then the excess molecules tend to self-associate in the bulk-solution forming micelles. This results in the invariant surface tension. The CMC for pure surfactants and surfactant-additive systems were determined by distinct breaks in the surface tension/specific conductivity versus concentration plots. The surface tension measurement technique has been found to be more advanced over conductometric technique, as small micellar aggregates can be detected by the former method. Here, we have given representative plots of surface tension versus log conc. of pure m-2-m (m = 10, 12, 14) (Fig. 1). The CMC values for pure gemini surfactants are in accordance with the reported literature values [21]. The determination of CMC and the other related parameters are dependent upon the methodology adopted and these values show variation by different methods. Therefore, we have taken average CMC values determined by tensiometry as well as conductometry for general correlation. Variation of CMC with salt concentration is presented in Fig. 2, which makes the role of coion/counterion quite evident with regard to CMC values.

Role of Co- and Counterions on the Micellization of Geminis

The CMC and counterion dissociation for the self-aggregating gemini in the presence of different fixed concentrations of salts of Na⁺, K⁺ and Li⁺ were determined at 303 K. The CMC forming efficiency order was K⁺ > Na⁺ > Li⁺. The charge on the counterion plays significant role in the micellization phenomenon. In Fig. 2a, the CMC values obtained are plotted against the added salt concentrations. Due to the synergistic effect, on increasing salt



Fig. 2 Values of CMC of the gemini surfactants m-2-m (m = 10, 12, 14) at different concentrations of a inorganic salts, and b organic salts

concentration, a decrease in CMC values of gemini surfactants is observed. This can be understood by considering the positive and negative contributing factors in the micellization process. The primary driving force in micellization is the hydrophobic effect associated with the alkyl chain association [10], which promotes the release of water molecules and solvates the apolar chain. Due to the hydrophobic effect or the assembly of the amphiphilic monomers, a net entropy increase in the system takes place. There is a balance between the electrostatic force among the amphiphilic headgroups with their counterions and water at the micellar surface. Neutral ion pairs are formed



Fig. 3 Correlation between the polarizability (p) and the CMC of 14-2-14+ inorganic salts (NaBr, NaNO₃, and NaCl)

by the positively charged headgroups and negatively charged counterions in solution that are less hydrated than free ions, which ultimately leads to the release of water into the bulk with the entropy increase. The more hydrophobic the counterion, the more strongly it interacts with an amphiphilic micellar interface (leading to stronger ion-pair formation), hence favoring micelle formation by reducing the CMC.

The position of an ion in the Hofmeister series (HS) is considered to depend upon its hydrated radius $(r_{\rm h})$, or polarizability (p) and charge. The hydrated radius of the anion is inversely proportional to its polarizability. An anion having large polarizability is expected to enhance the binding of the counterion at the micellar surface and also decreases the electrostatic repulsion between the headgroups of the surfactant molecules, thus increasing the tendency of micellization and lowering both the CMC and p. Therefore, a typical HS for anions is as follows: Ace $tate^- < Cl^- < NO_3^- < Br^- < ClO_4^- < I^- < CNS^-$ (the positions of the NO₃⁻ and Br⁻ ions are often switched in the HS) [30-32]. All the physical properties of the ions correlate well to the CMC as long as the ions have similar electronic configuration and similar morphologies. As the hydrated size of Cl⁻ is larger than that of Br⁻ [33], the mobility of the former is smaller, and its ability to increase micropolarity is weaker. The counterions are adsorbed at the positively charged head groups of the micelle. Less hydrated Br⁻ binds more strongly and, therefore, it can more strongly screen the interaction between gemini headgroups. Br⁻, with a larger diameter, has a stronger ability to suppress the Stern layer and reduces the curvature of the aggregate. Thus, the formation of larger aggregates is more favorable in the presence of NaBr. As a result, the CMC decrease is larger in NaBr than NaCl. As regards other physical properties of the ions, it has been found that the hydration number $(n_{\rm H})$ increases with the CMC, whereas the partial molar volume $(v_{\rm s})$, the polarizability (p) and the lyotropic number (N) decrease with increasing CMC [34–36]. In the present case too, a decrease in the CMC is found with the increasing polarizability of counterions (Fig. 3, where the polarizability (p) versus the CMC of 14-2-14 in the presence of 5 mM of NaBr, NaNO₃ and NaCl is plotted).

To extend our study further we have also chosen salts having an aromatic benzene ring in their structure (NaBenz, NaTos, NaSal, Scheme 2). These organic salts, also referred to as 'hydrotropes', are surface active and highly water soluble, which increase the solubility of solutes in water. Like surfactants, they have hydrophilic and short/cyclic hydrophobic groups. NaBenz contains a carboxylate group, NaSal contains a carboxylate and a hydroxyl group, whereas NaTos has a sulfonate group attached to the benzene ring. The difference in behavior can be explained by taking into account the structure, nature, and the relative basicity of the groups attached to these salts which leads to the following hydrophilic ranking [37].

$$-COO^{-} > -SO_{3}^{-}$$

As NaTos has a $-SO_3^-$, which is less hydrophilic than $-COO^-$ of NaBenz, the CMC decrease is slower with the former salt. It is well known that among different hydrotropes, NaSal is the most effective towards cationic surfactants [38]. Salicylate is the benzoate-derived counterion, which has a delocalized negative charge making it more hydrophobic (despite the presence of a hydrophilic –OH group). Salicylate has planar geometry which restricts the rotation of the carboxylate and further stabilizes the hydrogen bond. Due to this intramolecular hydrophobic [23]. The orientation of –COO⁻ (with respect to –OH) is responsible for the growth.

We can see that in the absence of salts, the CMC is not as lowered as in the presence of salts (Fig. 2b) which clearly indicates that at zero salt concentration, the surfactant molecules are not as tightly packed as when the micelles are formed in the presence of salts. In the absence of any salt counterion, the positively charged headgroups of gemini molecules tend to keep surfactant molecules away from each other due to electrostatic repulsion. As the addition of a salt takes place, a screening of the effective positive charges in the headgroup weakens the electrostatic repulsion. In addition, with cationic amphiphiles, Sal^{-/} Benz⁻ intercalates between the headgroups. The $-COO^$ group interacts with the positive charge of another micelle reducing its surface charge. In this way the micelles come closer to each other, making the hydrophobic interaction relatively stronger. Both these factors are responsible for lowering the CMC.

Ion-specificity is considered to be an important factor for micellar transition. A carboxylate headgroup is considered 'hard' and a sulfonate headgroup is considered as 'soft', therefore, their interactions with soft ammonium headgroups are different and thus hydrotropes can be compared to inorganic ions. This can be attributed to lower hydrophilicity of the sulfonate compared to the carboxylate moiety [39] or by a stronger interaction of the cationic surfactant headgroups with sulfonate groups compared to carboxylates as per their relative positions in the Hofmeister series [40]. There are two types of ions: 'hard' ions have high charge density and high polarizing power and 'soft' ions have low charge density and low polarizing power. According to the 'matching water affinity' concept of Collins [41], soft ions come into contact with soft ions and hard ions come into contact with hard ions. However, if hard ones come into contact with soft ions, they do not come into proximity and their hydration spheres remain intact, hence interacting weakly with each other. Therefore, such mixtures, where quaternary ammonium headgroups behave like soft ions, are responsible for enhancing the potential performance of gemini surfactants.

The reduction in CMC values in the case of the anionic hydrotropes and gemini surfactant systems indicates the existence of synergism between the two. An attractive interaction is operating between the two components. In addition to charge neutralization, intercalation of the hydrophobic part of the hydrotropes into gemini micelles also occurs. As can be seen (Scheme 2), all the hydrotropes used herein contain a hydrophobic benzene ring. Due to the interaction of the positively charged headgroup of the gemini with the π -electron cloud of the benzene ring, the hydrophobic interaction increases. Whereas, at high concentration of hydrotropes, due to higher interaction, the additional π - π aromatic interactions between the headgroups of hydrotropes are observed [42]. All these changes are responsible for enhancing the hydrophobic environment in the gemini-hydrotrope system (Scheme 3).

Thus, the reduction in CMC on addition of hydrotropes to gemini surfactant solutions is due to two important factors. The partitioning of hydrotropes and their adsorption on the headgroups of geminis (i) reduces the electrostatic repulsions, and (ii) enhances the hydrophobic character, thereby reducing the concentration where aggregation begins. Besides, the possibility of hydrogen bonding cannot be ignored.

Role of Spacer and Alkyl Chain Length in the Gemini Micellization

The micellization and adsorption properties of cationic gemini surfactants are strongly affected by the alkyl chain length and the nature of the spacer. For s = 2, as the distance between two alkyl chains is short, the hydrophobic interaction is promoted. As a result, the hydrophobic hydration is restricted and electrostatic repulsion is minimized between the two alkyl chains of the gemini molecules, producing lower CMC values. It can be inferred from the Table 1 data that, when we move from m = 10 to m = 14 (alkyl chain length), the hydrophobic interactions are considered to be a major driving force. During micelle formation, the water molecules in hydration shell around the hydrophobic parts of monomeric amphiphiles are released, also resulting in a greater entropy increase and giving rise to micellization at a lower concentration (lower CMC). With s remaining the same in the three gemini surfactants used herein, the decrease in CMC follows a behavior akin to the alkyl chain length effect of conventional surfactants.

Surface Properties

Scheme 3 Schematic representation of mixed micelle formation of cationic geminiorganic counterion (hydrotrope) Cationic gemini **Hydrotropes**

Gemini molecules are found to be more tightly packed at the interface and the γ_{CMC} decreases considerably with



systems

Table 1 Values of CMC, Π_{CMC} , Γ_{max} , A_{\min} , ΔG_{m}^0 and ΔG_{ads}^0 for gemini surfactant 14-2-14+ salt systems at 303 K

Additives (mM)	CMC (mM)	$\Pi_{CMC} \ (mN \ m^{-1})$	$\Gamma_{\rm max} \ 10^7 \ ({\rm mol} \ {\rm m}^{-2})$	A_{\min} (Å ²)	$\Delta G_{\rm m}^0~({\rm kJ~mol^{-1}})$	$\Delta G_{\rm ads}^0 ~({\rm kJ}~{\rm mol}^{-1})$
LiCl + 14-2-14						
0	0.118	35.41	7.66	217	-32.90	-37.52
0.5	0.098	37.56	8.33	199	-33.36	-37.87
1	0.087	37.66	8.41	197	-33.66	-38.14
2	0.058	38.14	9.54	174	-34.69	-38.69
3	0.053	39.58	9.97	167	-34.90	-38.87
5	0.044	43.83	10.50	158	-35.39	-39.56
NaCl + 14-2-14						
0.5	0.074	38.12	8.99	185	-34.06	-38.30
1	0.057	39.50	9.81	169	-34.71	-38.74
2	0.044	39.53	11.38	146	-35.39	-38.86
3	0.030	39.75	12.59	132	-36.31	-39.47
5	0.026	40.67	12.76	130	-36.71	-39.90
KCl + 14-2-14						
0.5	0.068	38.95	9.19	181	-34.27	-38.51
1	0.054	40.26	10.87	153	-34.87	-38.58
2	0.038	40.98	11.50	144	-35.72	-39.29
3	0.028	39.62	13.31	125	-36.53	-39.50
5	0.024	40.92	13.55	123	-36.92	-39.94
$NaNO_3 + 14-2-14$						
0.5	0.052	41.52	10.34	161	-34.97	-38.98
1	0.036	42.92	11.50	144	-35.86	-39.59
2	0.028	43.31	11.76	141	-36.48	-40.16
3	0.021	45.19	13.36	124	-37.25	-40.63
5	0.018	45.11	14.33	116	-37.64	-40.79
NaBr + 14-2-14						
0.5	0.050	41.20	12.27	135	-35.04	-38.40
1	0.035	42.02	13.25	125	-35.928	-39.10
2	0.024	43.12	14.36	116	-36.915	-39.92
3	0.018	41.04	14.45	115	-37.570	-40.41
5	0.015	43.96	15.36	109	-38.099	-40.96
NaTos + 14-2-14						
0.5	0.046	38.67	12.46	133	-35.25	-38.35
1	0.040	41.98	13.03	127	-35.63	-38.85
2	0.021	42.76	13.58	122	-37.25	-40.40
3	0.014	43.06	14.87	112	-38.18	-41.08
5	0.011	43.38	15.37	108	-38.77	-41.59
NaBenz + 14-2-14	4					
0.5	0.043	40.01	12.71	131	-35.45	-38.60
1	0.037	40.63	13.62	122	-35.79	-38.77
2	0.012	41.28	14.35	116	-38.56	-41.44
3	0.009	41.33	15.52	107	-39.39	-42.05
5	0.007	41.57	15.81	105	-40.02	-42.65
NaSal + 14-2-14						
0.5	0.029	35.52	13.08	127	-36.40	-39.11
1	0.024	35.57	14.63	114	-36.86	-39.29
2	0.009	36.70	14.67	113	-39.25	-41.75
3	0.007	36.88	16.28	102	-39.85	-42.11
5	0.006	36.71	16.66	100	-40.41	-42.61

increasing salt concentration. The variation of $\Pi_{\rm CMC}$ (the surface pressure at the CMC), $\Gamma_{\rm max}$ (the maximum surface excess), $A_{\rm min}$ (minimum surface area per molecule), $\Delta G^0_{\rm m}$ (the standard Gibbs energy of micellization) and $\Delta G^0_{\rm ads}$ (the standard Gibbs energy of adsorption) values, obtained at different concentrations of the added salts in 14-2-14 solutions, are collected in Table 1. However, for the other two geminis (10-2-10 and 12-2-12), these parameters are given in supporting information (Tables T1a, T1b). Detailed explanations for these parameters are given below.

Effect of Salt Counterions on Π_{CMC}

The Π_{CMC} values were obtained by using equation:

$$\Pi_{\rm CMC} = \gamma_0 - \gamma_{\rm CMC} \tag{1}$$

where γ_0 and $\gamma_{\rm CMC}$ are the surface tension of the solvent and the surface tension of the mixture at the CMC, respectively. With an increase in salt concentration, the increase in $\Pi_{\rm CMC}$ values indicates increased efficiency. The trend is as follows: 10-2-10 < 12-2-12 < 14-2-14 (Tables 1, TS1a, TS1b).

Effect of Salt Counterions on Γ_{max}

The Gibbs Eq. (2) [43] is used for calculating Γ_{max} of the gemini molecules at the air/water interface

$$\Gamma_{\text{max}} = (-1/2.303 \, nRT) (d\gamma/d\log C)_{\text{T}}$$
⁽²⁾

where *R* and *T* are the universal gas constant $(8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1})$ and temperature, respectively. The prefactor *n* is the number of species which are adsorbed at the air/water interface. In the present case, we have taken n = 3. The slope of the tangent at the given concentration of the γ versus log *C* plot was used to calculate Γ_{max} . The Γ_{max} values increase with an increase in salt concentration (Tables 1, TS1a, TS1b, Fig. 4). It can be inferred from the results that, in the presence of salts, the gemini surfactant molecules have a greater tendency to be adsorbed at the air/water interface, compared to that in the absence of salts. The presence of salts reduces the repulsion among head groups and more gemini surfactant molecules can be adsorbed at the interface. This can be directly related to the minimum area per headgroup (A_{\min}) values as given below.

Effect of Salt Counterions on A_{\min}

 A_{\min} is calculated using the equation:

$$A_{\rm min} = 10^{20} / N_{\rm A} \Gamma_{\rm max} \tag{3}$$

where N_A is Avogadro's number. Due to the effective charge shielding in the presence of salts and the tight packing of the

gemini surfactant ions at the micellar surface, the A_{min} value shows a decrease with increasing concentration of salts (Fig. 5). It also confirms that the gemini surfactant molecules are almost perpendicularly located at the micellar interface [44].

Effect of Salt Counterions on g-Values

Various factors play an important role in the addition of salt counterions. The present counterions in the solution are electrostatically attracted to the charged micelles and are adsorbed into the inner electrical double layer, partially neutralizing the surface charge. The extent of charge neutralization is known as counterion binding. The degree of dissociation (g) was obtained from the ratio of the post- and pre-CMC linear courses (using the conductance isotherms) by the relation, g = post-CMC slope/pre-CMC slope. It has been explained that the degree of dissociation (g) depends on the nature and concentration of added salts, the coions do not affect the values of g much. As the degree of counterion binding also depends upon the surface charge density of the micelle, the greater the charge density, the greater will be the counterion binding with a smaller surface area per head group. It shows no regular variation of g values (Supporting information, Fig. S1). The g values were found to increase with the increase in the salt concentration and this could be due to the reduction in the charge density on the micellar surface and release of counterions, while the decrease at still higher values of salt concentration may be due to higher counterion binding on the micelle surface.

Effect of Salt Counterions on the Thermodynamics of Micelle Formation

A thermodynamic description of the process of micelle formation includes a description of both electrostatic and hydrophobic contributions to the overall Gibbs energy of the system. The hydrophobic Gibbs energy (transfer Gibbs energy) is defined as Gibbs energy for the process of transferring the hydrocarbon solute from the hydrocarbon solvent to water. Micelle formation in an aqueous medium is a thermodynamically favored and a spontaneous process accompanied by a significant decrease in free energy, and the driving force behind it is the hydrophobic bonding accompanied by desolvation. Thus, the phenomenon of micellization is an energetically controlled process, where the formation of the micelle is well under thermodynamic control.

For all the geminis, the Gibbs free energy of micellization [45] was calculated using equation:

$$\Delta G_{\rm m}^0 = (3 - 2g) RT. \ln {\rm CMC}_{12} \tag{4}$$

In this equation, the CMC_{12} is the CMC of the mixture of the two components at a given mole fraction. For



Fig. 4 Values of Γ_{max} of the gemini surfactants m-2-m (m = 10, 12, 14) at different concentrations of **a** inorganic salts, and **b** organic salts



Fig. 5 Values of A_{\min} of the gemini surfactants m-2-m (m = 10, 12, 14) at different concentrations of **a** inorganic salts, and **b** organic salts

Depringer ACCS 🕉

surfactants with low CMC values (below 10 mM), the values of ΔG_m^0 would only differ by constant $\approx \ln 55.5$ when using one or the other unit [5] (for the micellization in pure water, the number of moles of solvent is taken as 55.5 mol dm⁻³). The negative values of the ΔG_m^0 indicate that micellization process is spontaneous in an aqueous medium (Table 1). The low CMC values of the m-2-m surfactants arise mainly because more than one chain is transferred simultaneously from background solvent to the micelle.

Further, the standard Gibbs energy of adsorption [46], ΔG_{ads}^0 is calculated using

$$\Delta G_{\rm ads}^0 = \Delta G_{\rm m}^0 - \Pi_{\rm CMC} / \Gamma_{\rm max} \tag{5}$$

The standard state for the adsorbed surfactant is a hypothetical monolayer at its minimum surface area per molecule, but at zero surface pressure. The last term in Eq. (5) expresses the work involved in transferring the surfactant molecule from a monolayer at a zero surface pressure to the micelle. All the negative values obtained imply that the adsorption of the surfactants at the air/water interface takes place spontaneously in the order: 10-2-10 < 12-2-12 < 14-2-14. The average values for ΔG_{ads}^0 for salts show the following trend: NaSal > NaBenz > NaTos > NaBr > NaNO₃ > KCl > NaCl > LiCl (Table 1), which is in accordance with our previous discussion.

Organic Salt Effect on Interaction Parameters

As reported earlier, organic salts have additional hydrophobic interactions besides an electrostatic one. They have a tendency to penetrate the micellar surface leading to micellar growth with lower loading of bulky organic counterions. An induction of strong hydrophobic interaction and reduction of electrostatic repulsion between the headgroups lead to the formation of tightly packed reduced curvature aggregates. Addition of hydrotropes (organic salts), bearing an opposite charge and hydrophobicity, reduces the electrostatic repulsion between the headgroups, whereas the hydrophobic interaction increases to the extent of being more with a surfactant having a larger alkyl chain length. As a result, more stable mixed systems with higher alkyl chain lengths of geminis are formed due to the synergistic interactions. Thus, a mixture of hydrotropes with gemini surfactants leads to the formation of mixed aggregates because of the different surface activity of the components.

Mixed micelles formed in the solutions of such nonhomogeneous surface active materials are expected to be nonideal. The nonideal mixing is quantified using Rubingh's model [47]. This model is based on Regular Solution Theory (RST) for nonideal mixed systems. In order to investigate interactions between two compounds at an interface or in micelles, the so-called β parameters (interaction parameters) are calculated by using Rubingh's and Rosen's approach [48], which are conveniently obtained from surface (or interfacial) tension or from CMC data by using the well-known Eqs. (6–9). By knowing the β parameters, the nature and strength of the interaction between the two components can be ascertained (β^{m} is the interaction parameter for mixed micelle formation in an aqueous medium and β^{σ} is the interaction parameter for mixed monolayer formation at an aqueous solution/air interface). The average CMC values of NaTos, NaBenz, and NaSal used in the calculation are 199.10, 290.17, 577.84 mM, respectively.

For mixed micellar systems the Rubingh's approach is applied as:

$$\frac{\left[\left(X_{1}^{m}\right)^{2}\ln\left(CMC_{12}\,\alpha_{1}/CMC_{1}X_{1}^{m}\right)\right]}{\left(1-X_{1}^{m}\right)^{2}\ln\left[CMC_{12}(1-\alpha_{1})/CMC_{2}\left(1-X_{1}^{m}\right)\right]} = 1 \quad (6)$$

$$\beta^{\rm m} = \frac{\ln({\rm CMC}_{12}\alpha_1/{\rm CMC}_1X_1^{\rm m})}{\left(1 - X_1^{\rm m}\right)^2} \tag{7}$$

(CMC₁, CMC₂, and CMC₁₂ denote the experimental CMC values of hydrotrope, surfactant, and their binary mixture, respectively, and $X_1^{\rm m}$ is the micellar mole fraction of the hydrotrope in the mixed micelle).

Analogously, for a mixed monolayer of micelles, Rosen's approach is applied as:

$$\frac{\left[\left(X_{1}^{\sigma}\right)^{2}\ln\left(\operatorname{conc}_{12}\alpha_{1}/\operatorname{conc}_{1}X_{1}^{\sigma}\right)\right]}{\left(1-X_{1}^{\sigma}\right)^{2}\ln\left[\operatorname{conc}_{12}(1-\alpha_{1})/\operatorname{conc}_{2}(1-X_{1}^{\sigma})\right]} = 1$$
(8)

$$\beta^{\sigma} = \frac{\ln\left(\operatorname{conc}_{12}\alpha_1/\operatorname{conc}_1 X_1^{\sigma}\right)}{\left(1 - X_1^{\sigma}\right)^2} \tag{9}$$

(where, conc₁, conc₂, and conc₁₂ denote the concentrations of hydrotrope, surfactant, and their binary mixture, respectively, and X_1^{σ} is the micellar mole fraction of the hydrotrope in the mixed micelle).

A positive β value signifies repulsive interaction among mixed species, whereas a negative value signifies an attractive interaction. The more negative values evidence strong interaction. In all the mixed systems, negative β^{m} values are obtained (Table 2, TS2a, TS2b, Fig. 6), which suggest that the interaction between the two components is more attractive in mixed micelles as compared to the selfinteraction of the two components before mixing. With an increasing mole fraction of hydrotropes, due to the intercalation of counterions in the gemini micelles, attractive as well as hydrophobic interactions increase and hence more negative β^{m} values and low CMC values are obtained. For the mixed monolayer (Rosen's approach), the β^{σ} values also show a similar trend (Table 2, TS2a, TS2b, Fig. 6), i.e., the salt-gemini mixtures have a stronger attractive interaction at the solution/air interface. Further, in most of the cases, with increase in alkyl chain length, the attractive interactions of organic salt-gemini systems increase.

The β values are related to the activity coefficients (f_i) in the mixed systems as per the following equations:

$$f_1^{\rm m} = \exp\left[\beta^{\rm m} \left(1 - X_1^{\rm m}\right)^2\right] \tag{10}$$

$$f_2^{\rm m} = \exp\left[\beta^{\rm m} \left(X_1^{\rm m}\right)^2\right] \tag{11}$$

$$f_1^{\sigma} = \exp\left[\beta^{\sigma} \left(1 - X_1^{\sigma}\right)^2\right] \tag{12}$$

$$f_2^{\sigma} = \exp\left[\beta^{\sigma} \left(X_1^{\sigma}\right)^2\right] \tag{13}$$

The activity coefficients of gemini surfactants (f_2) are found to be higher than that of the hydrotropes (f_1) (Table 2), which are less than unity, indicating nonideal behavior and synergistic interaction between the two components.

The greater the value of the interaction parameter, the greater the extent of nonideality in the system and the smaller the value of the activity coefficient. The low hydrophobicity and the higher CMC values, besides other factors, such as chain length and structure, also affect the interactions.

Conclusions

A comprehensive study of the ion specific effect of the salt counterions on the micellization of cationic gemini surfactants (m-2-m, m = 10, 12, 14) were performed by conductometric and tensiometric measurements: The micellization of gemini surfactants in the presence of salts occurs at lower concentrations. The inorganic counterions have been found to affect the micellization of geminis by obeying the Hofmeister series. The organic salts have been found to decrease the CMC more effectively than inorganic salts and the trend observed is found to be NaSalicylate > NaBenzoate > $NaTosylate > NaBr > NaNO_3 > KCl > NaCl > LiCl.$ With an increase in salt concentration, the increase in Π_{CMC} values indicates increased efficiency. The trend is as follows: 10-2-10 < 12-2-12 < 14-2-14. The A_{\min} value shows a decrease with an increasing concentration of salts. It also confirms that the gemini surfactant molecule is almost perpendicularly located at the micellar interface. The Γ_{max} values increase with an increase in salt concentrations, which confirm that in the presence of salts, the gemini surfactant molecules have a greater tendency to become adsorbed at the air/water interface, compared to that in the

Table 2 Micellar compositions (X_1^m, X_1^σ) , interaction parameters (β^m, β^σ) , and activity coefficients $(f_1^m, f_2^n, f_1^\sigma, f_2^\sigma)$ of binary mixtures of cationic gemini surfactant 14-2-14 at different mole fractions of salts at 303 K

α_{salt}	X_1^{m}	β^{m}	$10^4. f_1^m$	f_2^{m}	X_1^{σ}	β^{σ}	$10^4. f_1^{\sigma}$	f_2^{σ}
NaTos +	14-2-14							
0.5	0.289	-15.457	4.04	0.2750	0.290	-15.704	3.6464	0.2669
0.66	0.323	-17.014	4.11	0.1694	0.337	-18.840	2.5312	0.1177
0.8	0.370	-21.129	2.28	0.0554	0.376	-22.570	1.5245	0.0411
0.85	0.388	-23.344	1.60	0.0298	0.391	-24.399	1.1745	0.0239
0.9	0.405	-25.310	1.28	0.0158	0.406	-25.988	1.0419	0.0138
NaBenz -	+ 14-2-14							
0.5	0.289	-16.357	2.56	0.2550	0.291	-16.144	2.9891	0.2549
0.66	0.321	-17.858	2.66	0.1588	0.326	-17.930	2.9004	0.1488
0.8	0.377	-23.961	0.914	0.0332	0.383	-24.605	0.8550	0.0270
0.85	0.392	-25.989	0.673	0.0184	0.394	-25.782	0.7727	0.0183
0.9	0.407	-27.979	0.533	0.0097	0.410	-28.117	0.5616	0.0089
NaSal +	14-2-14							
0.5	0.301	-19.188	0.848	0.1758	0.282	-17.459	1.2336	0.2494
0.66	0.331	-20.954	0.845	0.1007	0.310	-18.648	1.3941	0.1667
0.8	0.375	-26.260	0.351	0.0249	0.366	-24.633	0.5009	0.0369
0.85	0.387	-27.850	0.285	0.0154	0.380	-26.326	0.4029	0.0223
0.9	0.401	-29.729	0.233	0.0084	0.394	-27.828	0.3646	0.0133

Fig. 6 Values of β^m , β^σ of the gemini surfactants m-2-m (m = 10, 12, 14) at different mole fractions (α_{salt}) of organic salts (NaSal, NaBenz, NaTos)



absence of salts. The negative values of the ΔG_m^0 indicate that micellization process is spontaneous in an aqueous medium. The average values for ΔG_{ads}^0 for salts show the following trend: NaSalicylate > NaBenzoate > NaTosylate > NaBr > NaNO₃ > KCl > NaCl > LiCl. All the negative values obtained imply that the adsorption of the surfactants at the air/water interface takes place spontaneously. In both the cases of $\Delta G_{\rm m}^0$ and $\Delta G_{\rm ads}^0$, more negative values are obtained with increasing alkylchain length of gemini and shows following trend: 10-2-10 < 12-2-12 < 14-2-14. Mixtures of hydrotropes (organic salts) with gemini surfactants lead to the formation of mixed aggregates because of the different surface activity of the components. With an increasing mole fraction of hydrotropes, due to the intercalation of salt counterions in the gemini micelles, the attractive interaction as well as hydrophobic interaction increase and hence more negative β^{m} values and low CMC values are obtained. For the salt-gemini mixtures, attractive interactions and X_1 values are nearly equal in mixed micelles and monolayers. Further, with an increase in alkyl chain length of gemini, the attractive interactions of organic salt-gemini systems increase. The activity coefficients of gemini surfactants (f_2) are found to be higher than those of the hydrotropes (f_1) , which are less than unity, indicating nonideal behavior and a synergistic interaction between the two components. The nature and the structure of salts primarily govern the morphology of the gemini. Thus, these systems may be utilized for tuning the micellar morphology or for reduction of CMC.

Acknowledgments USS and JA acknowledge CST-UP, Lucknow (CST-790) and UGC, respectively, for providing financial assistance. KU is grateful for UGC-BSR Faculty Fellowship award.

References

- 1. Rosen MJ (2004) Surfactants and interfacial phenomena. Wiley Interscience, New York
- Rosen MJ, Tracy DJ (1998) Gemini surfactants. J Surf Deterg 1:547–554
- 3. Zana R (1998) In: Holmberg K (ed) Novel surfactants. Marcel Dekker, New York
- Zana R, Benrraou M, Rueff R (1991) Alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactants. 1. Effect of the spacer chain length on the critical micelle concentration and micelle ionization degree. Langmuir 7:1072–1075
- Zana R (2002) Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review. Adv Colloid Interface Sci 97:205–253
- You Y, Zhao J, Jiang R, Cao J (2009) Strong effect of NaBr on self-assembly of quaternary ammonium gemini surfactants at air/ water interface and in aqueous solution studied by surface tension and fluorescence techniques. Colloid Polym Sci 287:839–846
- De S, Aswal VK, Goyal PS, Bhattacharya S (1996) Role of spacer chain length in dimeric micellar organization. Small angle neutron scattering and fluorescence studies. J Phys Chem 100:11664– 11671
- Han L, Chen H, Luo P (2004) Viscosity behaviour of cationic gemini surfactants with long alkyl chains. Surf Sci 564:141–148
- 9. Zana R, Talmon Y (1993) Dependence of aggregate morphology on structure of dimeric surfactants. Nature 362:228–230
- 10. Tanford C (1980) The hydrophobic effect: formation of micelles and biological membranes. Wiley, New York
- Wennerstrom H, Lindman B (1980) Micelles. Amphiphile aggregation in aqueous solution. Top Curr Chem 87:1–87
- 12. Zana R (1987) Surfactant solutions: new methods of investigation. Dekker, New York
- 13. Israelachvili JN (1992) Intermolecular and surface forces. Academic, London
- Hofmeister F (1888) About the science of the effect of salts. Arch Exp Pathol Pharmakol 24:247–260

- Romsted L, Yao J (1996) Arenediazonium salts: new probes of the interfacial compositions of association colloids. 4. 1–3 Estimation of the hydration numbers of aqueous hexaethylene glycol monododecyl ether, C12E6. Micelles by chemical trapping. Langmuir 12:2425–2432
- Romsted L (2007) Do amphiphile aggregate morphologies and interfacial compositions depend primarily on interfacial hydration and ion-specific interactions? The Evidence from chemical trapping. Langmuir 23:414–424
- Brady JE, Evans DF, Kachar B, Ninham BW (1984) Spontaneous vesicles. J Am Chem Soc 106:4279–4280
- Moroi Y, Murata Y, Fukuda Y, Kido Y, Seto W, Tanaka M (1992) Solubility and micelle formation of bolaform-type surfactants: hydrophobic effect of counterion. J Phys Chem 96: 8610–8613
- Bijma K, Engberts J (1997) Effect of counterions on properties of micelles formed by alkylpyridinium surfactants. 1. Conductometry and ¹H-NMR chemical shifts. Langmuir 13:4843–4849
- Debnath S, Dasgupta A, Mitra R, Das P (2006) Effect of counterions on the activity of lipase in cationic water-in-oil microemulsions. Langmuir 22:8732–8740
- Achouri MEl, Bensouda Y, Gouttaya HM, Nciri B, Perez L, Infante MR (2001) Gemini surfactants of the type 1,2-Ethanediylbis-(dimethylalkylammonium bromide). Tenside Surf Deterg 38:208–215
- Wattebled L, Laschewsky A (2007) Effects of organic salt additives on the behavior of dimeric ("Gemini") surfactants in aqueous solution. Langmuir 23:10044–10052
- Jiang L, Peng Y, Yan Y, Deng M, Wang Y (2004) Micellization of cationic gemini surfactants with various counterions and their interaction with DNA in aqueous solution. J Phys Chem B 108:15385–15391
- Manet S, Karpichev Y, Bassani D, Ahmad RK, Oda R (2010) Counteranion effect on micellization of cationic gemini surfactants 14-2-14: hofmeister and other counterions. Langmuir 26:10645–10656
- 25. Khan F, Siddiqui US, Khan IA, Kabir-ud-Din (2012) Physicochemical study of cationic gemini surfactant butanediyl-1,4-bis (dimethyldodecylammonium bromide) with various counterions in aqueous solution. Colloid Surf A 394:46–56
- Muller N, Birkhahn RH (1968) Investigation of micelle structure by fluorine magnetic resonance. II. Effects of temperature changes, added electrolyte, and counterion size. J Phys Chem 72:583– 588
- Paul BC, Islam SS, Ismail K (1998) Effect of acetate and propionate co-ions on the micellization of sodium dodecyl sulfate in water. J Phys Chem B 102:7807–7812
- Zana R, Levy H (1997) Alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactants (dimeric surfactants) Part 6. CMC of the ethanediyl-1,2-bis(dimethylalkylammonium bromide) series. Colloid Surf A 127:229–232
- Sun Y, Feng Y, Dong H, Chen Z, Han L (2007) Synthesis and aqueous solution properties of homologous gemini surfactants with different headgroups. Central Eur J Chem 5:620–634
- Kunz W, Nostro PLo, Ninham BW (2004) The present state of affairs with Hofmeister effects. Curr Opin Colloid Interface Sci 9:1–18
- Vlachy N, Cwiklik BJ, Vácha R, Touraud D, Jungwirth P, Kunz W (2009) Hofmeister series and specific interactions of charged headgroups with aqueous ions. Adv Colloid Interface Sci 146: 42–47
- Vlachy N, Drechsler M, Touraud D, Kunz W (2009) Anion specificity influencing morphology in catanionic surfactant mixtures with an excess of cationic surfactant. C R Chim 12:30–37
- Nightangle ER Jr (1959) Phenomenological theory of ion solvation. Effective radii of hydrated ions. J Phys Chem 63:1381–1387

- 34. Mukerjee P, Karematsu K, Obawauchi M, Sugihara G (1985) Effect of temperature on the electrical conductivity and the thermodynamics of micelle formation of sodium perfluorooctanoate. J Phys Chem 89:5308–5312
- Rodriguez JR, Perez AG, Castillo JLD, Czapkiewicz J (2002) Thermodynamics of micellization of alkyldimethylbenzylammonium chlorides in aqueous solutions. J Colloid Interface Sci 250:438–443
- Rosen MJ (2004) Surfactants and interfacial phenomena. Wiley, New York, p 215
- Naqvi AZ, Rub MA, Kabir-ud-Din (2011) Effects of pharmaceutical excipients on cloud points of amphiphilic drugs. J Colloid Interface Sci 361:42–48
- Rao URK, Manohar C, Valaulikar BS, Iyer RM (1987) Micellar chain model for the origin of the viscoelasticity in dilute surfactant solutions. J Phys Chem 91:3286–3291
- Laughlin RG (1981) HLB from a thermodynamic perspective. J Soc Cosmet Chem 32:371–392
- Cacace MG, Landau EM, Ramsden JJ (1997) The Hofmeister series: salt and solvent effects on interfacial phenomena. Q Rev Biophys 30:241–277
- Collins KD (2004) Ions from the Hofmeister series and osmolytes: effects on proteins in solution and in the crystallization process. Methods 34:300–311
- 42. Haldar J, Aswal VK, Goyal PS, Bhattacharya S (2004) Aggregation properties of novel cationic surfactants with multiple pyridinium headgroups. Small-angle neutron scattering and conductivity studies. J Phys Chem B 108:11406–11411
- Chattoraj DK, Birdi KS (1984) Adsorption and the Gibbs surface excess. Plenum, New York
- 44. Ananda K, Yadav OP, Singh PP (1991) Studies on the surface and thermodynamic properties of some surfactants in aqueous and water +1, 4-dioxane solutions. Colloids Surf 55:345–348
- 45. Evans DF, Wennestorm H (1994) The colloidal domain: where physics, chemistry and biology meet. VCH, New York

- 46. Rosen MJ, Cohen AW, Dahanayake M, Hua X (1982) Relationship of structure to properties in surfactants. 10. Surface and thermodynamic properties of 2-dodecyloxypoly(ethenoxyethanol)s, $C_{12}H_{25}(OC_2H_4)_xOH$, in aqueous solution. J Phys Chem 86:541–545
- 47. Rubingh DN (1979) Mixed micelle solutions. In: Mittal KL (ed) Solution Chemistry of Surfactants, vol 1. Plenum, New York
- Rosen MJ (1998) Molecular interaction and the quantitative prediction of synergism in the mixtures of surfactants. Prog Colloid Polym Sci 109:35–41

Author Biographies

Jeenat Aslam is currently a Ph.D. student in the Department of Chemistry, Aligarh Muslim University, Aligarh, India. She received her M.Sc. degree from the same university.

Umme Salma Siddiqui is currently working as a Young Scientist in the Department of Chemistry, Aligarh Muslim University, Aligarh, India in a CST-UP, Lucknow, funded project (CST-790). She received her M.Sc. and Ph.D. degrees from the same university.

Wajid Husain Ansari received his M.Sc., M. Phil. and Ph.D. degrees from Aligarh Muslim University.

Kabir-ud-Din is currently a UGC-BSR Faculty Fellow at Aligarh Muslim University. He received his M.Sc. and Ph.D. degrees from the same university. He held postdoctoral positions at the universities in Prague (Czech Republic), Keele (UK) and Austin (USA). His present lines of research are micellar kinetics, electrochemistry, physicochemical behavior of micellar solutions, clouding phenomenon in amphiphilic systems, and so on.